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STUDY OF BONDING BETWEEN GLASS AND PLASTIC IN GLASS-REINFORCED
PLASTICS - EXTENDED WORK

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INTRODUCTION

The general objective of this research program is to evaluate the effect of deliberate and known chemical bonding between the glass reinforcement and the plastic matrix of a glass-reinforced plastic composite material.

Previous reports^{1,2} described studies of the methods by which siliceous surfaces can be modified with organic groups that are bonded to surface-based silicon atoms by silicon-carbon bonds. These surface-modifying organic groups can be chosen for specific interaction with the resin matrix of the composite material. Surface modification was accomplished in two steps:

- (1) Reactive-intermediate groups such as chlorine atoms (Cl), fluorine atoms (F), or alkoxyl groups (OR) were bonded to surface-based silicon atoms
- (2) Reactive-intermediate groups were converted to surface-modifying organic groups by reaction with an organometallic compound.

The objectives of the present phase of this project are: First, to evaluate the effects of surface modification upon a realistic composite material (such as a filament-wound NOL ring or a woven glass cloth laminate); second, to study optimum characteristics for surface-modifying groups and improved methods for obtaining them; and last, to study methods for application of surface modification to reinforcement materials other than glass and silica.

This is the third quarterly report for the current phase of work.

¹D. L. Chamberlain, Jr., A Study of Bonding Between Glass and Plastic in Glass-Reinforced Plastics, Phase I, Summary Technical Report No. 1, Contract NASr-49(14), July 31, 1964.

²D. L. Chamberlain, Jr., A Study of Bonding Between Glass and Plastic in Glass-Reinforced Plastics, Phase II, Summary Technical Report No. 2, Contract NASr-49(14), November 15, 1965.

DISCUSSION

Production of Test Specimens

NOL-Rings. The Parametrics NOL ring-winder has been received. The spool holders and pronny brake were missing. This work will be continued upon receipt of the items.

181-Cloth Laminates. The choice of a system for preparing test laminates has been made. Test laminates of 6 in. x 6 in. x 0.125 in. (12 ply) construction will be prepared from fluorinated 181 cloth, laminated with Epon 825-Nadic Methyl Anhydride resin. N-Benzyldimethylamine will be used as the initiator.

Cloth will be fluorinated in 6 in. wide strips hung on a rack, in a steel chamber 10 in. I.D. x 15 in. long. Cloth sufficient for two 12-ply laminates may be fluorinated at one time. The fluorination apparatus is now under construction and should be ready for use very soon.

Surface Modification Studies

Fluorination of Glass and Silica. Previously, the validity of fluoride analyses was in doubt because of unknown amounts of hydrogen fluoride in the fluorine gas. Hydrogen fluoride was removed by passage through a potassium fluoride absorption column. Fluorination of Cab-O-Sil with HF-free F_2 erased these doubts. Infrared spectra of the product showed an intense Si-F band at 939 cm^{-1} . This was confirmed by the appearance of a very strong Si-phenyl band at 1427 cm^{-1} upon alkylation with phenyllithium. The fluoride content of this sample corresponded to 5.3 fluorine atoms/100 \AA^2 (70% coverage).

A series of glass microscope slides was fluorinated to define the optimum procedure for carrying out the fluorination process. The results confirmed previous work and led to the following procedure of heating the sample in a nitrogen-filled reactor to 200°C and 20 psig. The reactor is bled to atmospheric pressure and is repressurized

to 20 psig with F_2 gas. Constant temperature and pressure are maintained for two hours. The reactor, still at operating temperature, is vented to atmospheric pressure and flushed with dry nitrogen by alternately pressurizing and venting. The reactor is then cooled to room temperature under a positive pressure of nitrogen gas, and the sample is removed and used without further treatment.

Alkylation Reactions. A series of halogenated Cab-O-Sil samples was alkylated with selected organometallics to gain information about the generation of organic surface groups with terminal substituents that may undergo reaction with the resin phase. The data on these samples are summarized in Table I.

The methyl derivative (No. 1, Table I) was included for comparison.

The allyl derivative (No. 2) will not be used, as such, in the present work. However, it does provide a pathway for preparation of a diol (No. 3) and a terminal alcohol (No. 4). Either one of these products should be useful for interaction with an epoxy resin.

The terminal carboxyl group on a 5-carbon chain (No. 5) should be useful for interaction with a polyester resin, but it will not be used in the present work with epoxy resin.

The terminal hydroxyl group on a 5-carbon chain (No. 6) was prepared from the same intermediate (pentane-1,5-dimagnesium bromide) as the carboxyl-terminated derivative. Air oxidation was accomplished by decantation of the Grignard solution, suspension of the silica in dry tetrahydrofuran, and bubbling of oxygen through the suspension. The yield was certainly not optimum. This derivative should be very useful in preparing epoxy laminates and will be used for the initial test laminate in the present work.

The population of surface-modifying groups on the reinforcement phase, required to achieve adequate bonding to the resin phase, is not known and must be determined by experience. One may calculate, however, a theoretical breaking strength for a given population (or concentration) of silicon-carbon linkages at the glass-resin interface. Assuming a

Table I
ALKYLATION REACTIONS OF CHLORINATED CAB-O-SIL

Reagent	Solvent	Product (-Si = silicon atom in silica surface)	Carbon Analysis Groups per 100 Å ²	Remarks
1 Methyl- magnesium iodide	diethyl ether	$\begin{array}{c} \\ -\text{Si}-\text{CH}_3 \\ \end{array}$	3.11	Cab-O-Sil was methoxylated instead of chlorinated.
2 Allyl- magnesium bromide	diethyl ether	$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ -\text{Si}-\text{CH}_2-\text{C}=\text{CH} \\ \end{array}$	1.43	IR spectra showed the $\begin{array}{c} \\ -\text{C}=\text{C}- \\ \end{array}$ band at 1625 cm ⁻¹ .
3 Peracetic acid epoxidation of material from (2)	acetic acid	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{O} \\ \quad \quad \\ -\text{Si}-\text{CH}_2-\text{C}-\text{C}-\text{OC}-\text{CH}_3 \\ \quad \quad \\ \text{O} \quad \text{H} \quad \text{H} \end{array}$	1.73	The desired product was -Si-CH ₂ -CH-CH ₃ . IR analysis OH OH indicated that the ester inter- mediate was not hydrolyzed; some adsorbed molecules probably were present.
4 Hydroboration product of (2) with BF ₃ and KBH ₄	diethylene glycol di- methylether	$\begin{array}{c} \\ -\text{Si}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{OH} \\ \end{array}$	1.43 (assumed from start- ing material)	IR spectra showed loss of -C=C- band at 1625 cm ⁻¹ . The original surface population was assumed to be unchanged.
5 Pentane-1,5- di-magnesium bromide	tetrahydro- furan	$\begin{array}{c} \\ -\text{Si}-(\text{CH}_2)_5-\text{C}-\text{O}-\text{H} \\ \\ \text{O} \end{array}$	0.7	The carboxyl group was obtained by carbonation of initial Grignard product. Carboxyl group was seen at 1710 cm ⁻¹ in IR spectrum.
6 Same as (5)	tetrahydro- furan	$\begin{array}{c} \\ -\text{Si}-(\text{CH}_2)_5-\text{OH} \\ \end{array}$	---	Alcoholic group was obtained by oxidation of initial Grignard product.

population of only one group per 100 Å², 60 kcal per mole for the Si-C bond, and a separation at the interface of 4 Å required for "bond breakage," a calculated bond strength of 150,000 psi is obtained. This "calculated bond strength" for only a 15% conversion (one out of 7.5) of available surface sites is very respectable and is considerably greater than the bulk strength of the plastic phase.

Analytical Studies

Carbon Analyses. Carbon on inorganic solid substrates can now be determined with a precision of ± 2 ppm of carbon. This can be done with the Leco Analyzer, which consists of the Leco Model 521 high-frequency induction furnace and the Leco Model 515 conductometric carbon analyzer. These components were completely renovated. Copper and aluminum tubing replaced rubber and Tygon tubing for oxygen and carbon dioxide lines. Nylon Swagelok fittings were used, instead of Tygon tubing, for connection of metal and glass lines. Teflon tubing was used to replace Tygon tubing for transporting conductivity solutions. The apparatus was standardized against carbon standards in the 30 to 210 ppm range.

Infrared Studies. As reported in the last quarterly report,³ the disappearance of surface OH groups, as measured by the infrared O-H stretching peak at 3757 cm⁻¹, was a useful indication of the extent of surface chlorination. The replacement of surface OH groups by Cl atoms resulted in the displacement of the 1080 cm⁻¹ Si-O stretching band in Cab-O-Sil silica. This method of observing the effect of surface modifications upon the lattice bonds of an inorganic substrate was developed in a related project⁴ for the study of adhesion mechanisms. The significance of lattice shifts due to absorption and chemical reactions is not fully understood, but it appears to have a basic relation to interfacial reactions. Therefore, some effort was devoted to examination of surface-modified silica.

³D. L. Chamberlain, Jr., Study of Bonding Between Glass and Plastic in Glass-Reinforced Plastics, Quarterly Progress Report No. 8, Dec. 28, 1966 Contract No. NASr-49(14).

⁴D. L. Chamberlain, Jr., M. Bertolucci, and M. V. Christensen, Mechanism of Adhesion to Teeth, Progress Report for the Seventh Quarter of Work, Contract No. A2(230)PH43-65-82, January 25, 1967.

This work will be reported in more detail in the next report.

Dilatometry

Dilatometry experiments were continued with a series of samples chosen to evaluate the effect of chemical bonding between an amine-modified silica and a polyurethane resin. Two low-iron silica samples were alkylated with ethyleneimine: a preparation in which no catalyst was used gave a silica with 18.9 ppm of carbon, which corresponds to about 2.2 ethyleneimine groups/100 Å²; a preparation in which boron trifluoride-etherate was used as a catalyst gave a silica containing 407 ppm of carbon. The carbon on this last sample could not be removed appreciably by water, chloroform, or methanol. Therefore, this product appears to contain homopolymer bound to the silica, since pure low-molecular weight poly(ethyleneimine) is soluble in methanol and water.

The Si-O-CH₂-CH₂-NH₂ group on silica, resulting from alkylation of silica ethyleneimine, will permit ready incorporation into a polyurethane resin and will provide a chemical link to the silica substrate. Since the physical tests will be carried out in a dry environment, no trouble is expected from the hydrolytically labile Si-O-C linkage. A comparison of these samples with control samples should provide an evaluation of the effect of surface modification upon interfacial bond strength.

The dilatometric measurement was unsuccessful due to failure of the load cell and failure of the adhesive joint between the end tabs and the sample. Another attempt to evaluate ethyleneimine-modified silica or glass is planned.

FUTURE WORK

Future efforts will emphasize final laminate preparation and evaluation.

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